1.0 Introduction

The objective of this two volume report is to provide a reasoned and documented discussion on the technical issues associated with the measurement of partition (or distribution) coefficient, K_d,[1,2] values and their use in formulating the contaminant retardation factor, R_f. Specifically, it describes the rate of contaminant transport relative to that of groundwater. The retardation factor is the empirical parameter commonly used in transport models to describe the chemical interaction between the contaminant and geological materials (*i.e.*, soils, sediments, and rocks). *Throughout this report, the term "soil" will be used as general term to refer to all unconsolidated geologic materials*.[3] The contaminant retardation factor includes processes such as surface adsorption, absorption into the soil structure, precipitation, and physical filtration of colloids. This report is provided for technical staff from EPA and other organizations who are responsible for prioritizing site remediation and waste management decisions.

Volume I contains a detailed discussion of the K_d concept, its use in fate and transport computer codes, and the methods for the measurement of K_d values. The focus of Chapter 2 is on providing an understanding of (1) the use of K_d values in formulating R_f, (2) the difference between the original thermodynamic K_d parameter derived from the ion-exchange literature and its "empiricized" use in contaminant transport codes, and (3) the explicit and implicit assumptions underlying the use of the K_d parameter in contaminant transport codes.

The K_d parameter is very important in estimating the potential for the adsorption of dissolved contaminants in contact with soil. As typically used in fate and contaminant transport calculations, the K_d is defined as the ratio of the contaminant concentration associated with the solid to the contaminant concentration in the surrounding aqueous solution when the system is at equilibrium. Soil and geochemists knowledgeable of sorption processes in natural environments have long known that generic or default K_d values can result in significant error when used to predict the absolute impacts of contaminant migration or site-remediation options. Therefore, for site-specific calculations, K_d values measured at site-specific conditions are absolutely essential.

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[1]   Throughout this report, the term "partition coefficient" will be used to refer to the K_d "linear isotherm" sorption model. It should be noted, however, that the terms "partition coefficient" and "distribution coefficient" are used interchangeably in the literature for the K_d model.

[2]   A list of acronyms, abbreviations, symbols, and notation is given in Appendix A. A list of definitions is given in Appendix B

[3]   The terms "sediment" and "soil" have particular meanings depending on one's technical discipline. For example, the term "sediment" is often reserved for transported and deposited particles derived from soil, rocks, or biological material. "Soil" is sometimes limited to referring to the top layer of the earth's surface, suitable for plant life. In this report, the term "soil" was selected as a general term to refer to all unconsolidated geologic materials.

To address some of this concern when using generic or default K_d values for screening calculations, modelers often incorporate a degree of conservatism into their calculations by selecting limiting or bounding conservative K_d values. For example, the most conservative estimate from an off-site risk perspective of contaminant migration through the subsurface natural soil is to assume that the soil has little or no ability to slow (retard) contaminant movement (*i.e.*, a minimum bounding K_d value). Consequently, the contaminant would migrate in the direction and, for a K_d value of ≈ 0, travel at the rate of water. Such an assumption may in fact be appropriate for certain contaminants such as tritium, but may be too conservative for other contaminants, such as thorium or plutonium, which react strongly with soils and may migrate 10^2 to 10^6 times more slowly than the water. On the other hand, to estimate the maximum risks (and costs) associated with on-site remediation options, the bounding K_d value for a contaminant will be a maximum value (*i.e.*, maximize retardation).

The K_d value is usually a measured parameter that is obtained from laboratory experiments. The general methods used to measure K_d values (Chapters 3 and 4) include the laboratory batch method, *in-situ* batch method, laboratory flow-through (or column) method, field modeling method, and K_{oc} method. The ancillary information needed regarding the adsorbent (soil), solution (contaminated ground-water or process waste water), contaminant (concentration, valence state, speciation distribution), and laboratory details (spike addition methodology, phase separation techniques, contact times) are summarized. The advantages, disadvantages, and, perhaps more importantly, the underlying assumptions of each method are also presented.

A conceptual overview of geochemical modeling calculations and computer codes as they pertain to evaluating K_d values and modeling of adsorption processes is discussed in detail in Chapter 5. The use of geochemical codes in evaluating aqueous speciation, solubility, and adsorption processes associated with contaminant fate studies is reviewed. This approach is compared to the traditional calculations that rely on the constant K_d construct. The use of geochemical modeling to address quality assurance and technical defensibility issues concerning available K_d data and the measurement of K_d values is also discussed. The geochemical modeling review includes a brief description of the EPA's MINTEQA2 geochemical code and a summary of the types of conceptual models it contains to quantify adsorption reactions. The status of radionuclide thermodynamic and contaminant adsorption model databases for the MINTEQA2 code is also reviewed.

The main focus of Volume II is to: (1) provide a "thumb-nail sketch" of the key geochemical processes affecting the sorption of a selected set of contaminants; (2) provide references to related key experimental and review articles for further reading; (3) identify the important aqueous- and solid-phase parameters controlling the sorption of these contaminants in the subsurface environment under oxidizing conditions; and (4) identify, when possible, minimum and maximum conservative K_d values for each contaminant as a function key geochemical processes affecting their sorption. The contaminants chosen for the first phase of this project include chromium, cadmium, cesium, lead, plutonium, radon, strontium, thorium, tritium (^{3}H), and uranium. The selection of these contaminants by EPA and PNNL project staff was based on two

criteria. First, the contaminant had to be of high priority to the site remediation or risk assessment activities of EPA. Second, due to budgetary constraints, a subset of the large number of contaminants that met the first criteria were selected to represent categories of contaminants based on their chemical behavior. The six nonexclusive categories are:

- Cations - cadmium, cesium, lead, plutonium, strontium, thorium, and uranium
- Anions - chromium(VI) (as chromate)
- Radionuclides - cesium, plutonium, radon, strontium, thorium, tritium (^{3}H), and uranium
- Conservatively transported contaminants - tritium (^{3}H) and radon
- Nonconservatively transported contaminants - other than tritium (^{3}H) and radon
- Redox sensitive elements - chromium, lead, plutonium, and uranium

The general principles of geochemistry discussed in both volumes of this report can be used to estimate the geochemical interactions of similar elements for which data are not available. For example, contaminants present primarily in anionic form, such as Cr(VI), tend to adsorb to a limited extent to soils. Thus, one might generalize that other anions, such as nitrate, chloride, and U(VI)-anionic complexes, would also adsorb to a limited extent. Literature on the adsorption of these 3 solutes show no or very little adsorption.

The concentration of contaminants in groundwater is controlled primarily by the amount of contaminant present at the source; rate of release from the source; hydrologic factors such as dispersion, advection, and dilution; and a number of geochemical processes including aqueous geochemical processes, adsorption/desorption, precipitation, and diffusion. To accurately predict contaminant transport through the subsurface, it is essential that the important geochemical processes affecting contaminant transport be identified and, perhaps more importantly, accurately described in a mathematically defensible manner. Dissolution/precipitation and adsorption/desorption are usually the most important processes affecting contaminant interaction with soils. Dissolution/precipitation is more likely to be the key process where chemical nonequilibium exists, such as at a point source, an area where high contaminant concentrations exist, or where steep pH or oxidation-reduction (redox) gradients exist. Adsorption/desorption will likely be the key process controlling inorganic contaminant migration in areas where the naturally-present constituents are already in equilibrium and only the anthropogenic constituents (contaminants) are out of equilibrium, such as in areas far from the point source. Diffusion flux spreads solute via a concentration gradient (*i.e.*, Fick's law). Diffusion is a dominant transport mechanism when advection is insignificant, and is usually a negligible transport mechanism when water is being advected in response to various forces.